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(54) **SOLS REFRIGERANTS DE FAIBLE VISCOSITE A PROPRIETES ANTICORROSION AMELIOREES**

(54) **LOW-VISCOSITY REFRIGERATING BRINES WITH IMPROVED CORROSION CONTROL**

(57) L'invention concerne des sols réfrigérants aqueux de faible viscosité, à base d'acétates et/ou de formiates de métaux alcalins inhibés, à propriétés anticorrosion améliorées, caractérisés en ce que les sols réfrigérants renferment 0,2 à 5 % en poids de sulfites ou de pyrosulfite de métaux alcalins, en particulier 1 à 2,5 % de ce sulfite. Les sols selon l'invention renferment en outre 0,3 à 5 % en poids de substances basiques appartenant au groupe des carbonates, hydroxydes, borates et phosphates alcalins, ainsi que 0 à 0,3 % en poids de silicates alcalins et 0,02 à 0,2 % en poids de stabilisants du groupe triazole, benzimidazole et/ou mercaptothiazole. Les nouveaux sols réfrigérants ont de très faibles vitesses de corrosion, notamment pour l'acier et la fonte.

(57) The invention relates to low-viscosity, aqueous refrigerating brines based on alkali metal acetates and/or formates with improved corrosion control. Said refrigerating brines are characterized in that they contain 0.2-5 wt.% alkali metal sulfites or pyrosulfites, in particular 1-2.5 wt.% of these sulfites. The inventive brines contain in addition: 0.3-5 wt.% alkaline substances from the alkali carbonate, hydroxide, borate and phosphate groups, as well as 0-0.3 wt.% alkali silicate and 0.02-0.2 wt.% stabilizers from the triazole, benzimidazole and/or mercaptothiazole groups. The novel refrigerating brines have very low corrosion rates, in particular in the case of steel and cast iron.

(57) **Abstract**

The invention relates to low-viscosity, aqueous refrigerating brines based on alkali metal acetates and/or formates with improved corrosion control. Said refrigerating brines are characterized in that they contain 0.2–5 wt.% alkali metal sulfites or pyrosulfites, in particular 1–2.5 wt.% of these sulfites. The inventive brines contain in addition: 0.3–5 wt.% alkaline substances from the alkali carbonate, hydroxide, borate and phosphate groups, as well as 0–0.3 wt.% alkali silicate and 0.02–0.2 wt.% stabilizers from the triazole, benzimidazole and/or mercaptothiazole groups. The novel refrigerating brines have very low corrosion rates, in particular in the case of steel and cast iron.

Low-viscosity coolant brines having improved corrosion protection

Coolant brines based on aqueous solutions of organic salts have a markedly lower viscosity than brines based on ethylene glycol or propylene glycol, in particular at low temperatures in the range from -20 to -40 °C. A further advantage is their physiological acceptability, such that they can be preferably employed in the foodstuffs sector for indirect cooling (for example freeze-drying, deep-freeze cabinets). A high water content of over 40% by weight renders the brines nonflammable. Due to the low viscosity, considerable energy savings can be achieved by recirculation. Due to the high water content, advantageous heat technology and refrigeration properties are additionally achieved, for example a high specific heat and a high heat transfer coefficient.

DE-A-44 12 954 (EP-A-0 677 563) proposes aqueous potassium formate solutions, which contain up to 55% by weight of formate and are utilizable to -55 °C, as coolants. As an inhibitor, these brines contain 1,2,4-triazole and/or borax. In the absence of borax, a pH indicator, preferably phenolphthalein, is added for control of the pH. DE-A-41 07 442 describes functional fluids, which essentially contain potassium acetate and potassium carbonate as an aqueous solution and which are inhibited against corrosion using small amounts of potassium fluoride, alkali metal salts of silicic acids and known inhibitors, for example benzotriazole, as heat transfer media and coolants.

A great problem of the cooling fluids mentioned is the corrosion of metallic materials caused by oxygen, in particular the corrosion of ferrous metals (iron, nickel, cobalt). Even if the cooling system is carefully flushed with nitrogen, in practice it can hardly be avoided that in the relatively long term air forces its way in again. The customary inhibitors from the silicates, phosphates and aromatic triazoles group in the long term are not effective enough in order to protect components made of ferrous metals, in particular of steel or gray iron.

Whereas concentrated aqueous solutions having a content of more than 40% by weight of potassium formate or potassium acetate, which contain the inhibitors mentioned, as a rule have a less corrosive action, this does not apply to dilute solutions. On increasing dilution with water, formic acid is formed from formates and acetic acid is formed from acetates by hydrolysis, which finally leads to a fall in the pH value and an increase in the corrosion rate.

The present invention relates to aqueous, low-viscosity coolant brines which contain metal salts of short-chain carboxylic acids, potassium formate and/or potassium acetate being preferred. As a rule, the salt content is between 20 and 60% by weight, depending on the degree of frostproofing desired. It was the object of the invention to find a coolant which has a good corrosion protection even in aqueous dilution in a frostproofing range from -10 to -40 °C. A further aim was to make it possible for the user to prepare a ready-to-use coolant brine according to its antifreeze specification by simple mixing of a concentration with a high degree of frostproofing and water. Thus it should also be avoided that the user would have to add a specially formulated inhibitor batch for each adjustment to a specific degree of frostproofing. The inhibitors added to the concentration should themselves have an antifreeze action without significantly increasing the viscosity. This is achieved according to the invention in that an effective amount of a sulfite is admixed to the coolant based on potassium formate and/or acetate, it surprisingly being found that the sulfites added still dissolved completely in an amount from 0.2 to 5, preferably 0.5 to 3, in particular 1.5 to 2.5, % by weight even at -40 °C. Within the sulfite group, alkali metal sulfites are preferred, in particular sodium sulfite and potassium sulfite. However, it is also possible to employ acidic sulfites (bisulfites, pyrosulfites) which as a rule are more highly soluble than the normal sulfites. As an additional protective measure, it is advisable to inertize the closed coolant circulation with nitrogen in order to avoid oxidation of the sulfite or hydrogen sulfite.

Additionally, alkaline substances such as, for example, potassium

carbonate, sodium carbonate, potassium hydroxide solution and/or sodium hydroxide solution, potassium phosphates and borax are added to the coolant brines according to the invention to increase the pH in order still to guarantee an adequate reserve alkalinity even on dilution of the abovementioned concentrations. The added amounts required are between 0.3 and 5% by weight. Furthermore, known nonferrous metal inhibitors for copper, gunmetal and brass from the triazoles, imidazoles, benzotriazoles (preferably 1,2,4-benzotriazole, 1H-benzotriazole) and the mercaptobenzothiazoles group are employed in amounts from 0.02 to 0.2% by weight. To improve the corrosion protection on aluminum materials, it is possible to use silicates, for example sodium metasilicate, waterglass and potassium silicates in an amount of up to 0.3% by weight.

To test the corrosion behavior, the examination which is widespread in industry as specified in ASTM D 1384-94 is used, which is carried out over a period of 336 h while passing through atmospheric oxygen (6 l of air/h) at a temperature of 88 °C. This simulates not only the unavoidable access of air into the coolant brine, but also the behavior at higher temperatures. As is known, refrigeration plants must be defrosted at regular intervals, which can be brought about by means of a so-called warm brine, that is using a brine of a temperature from +50 to +80°C.

The following examples show the composition and the corrosion behavior in the above ASTM test in undiluted form and on dilution with demineralized water. For comparison, the corrosion values without the addition of sulfites according to the invention are shown (Comparison Examples 1 to 4). Percentage data relate - if not stated otherwise - to percentages by weight. The difference to 100% by weight is in each case demineralized water.

Example 1

46%	of potassium acetate
3%	of potassium carbonate
1%	of sodium sulfite
0.05%	of potassium phosphate
0.1%	of 1H-tolyltriazole
0.05%	of 1H-benzotriazole

Comparison Example 1 (prior art)

46%	of potassium acetate
3%	of potassium carbonate
0.05%	of potassium phosphate
0.1%	of 1H-tolyltriazole
0.05%	of 1H-benzotriazole

Corrosion values according to ASTM D 1384-94 (material removed in g/m²)

	Example 1		Comparison Example 1	
Metal	undiluted	diluted 1:1	undiluted	diluted 1:1
Copper	-1.0	-1.3	-1.4	- 1.2
Brass	-2.3	-2.0	-3.0	- 1.8
Steel	-2.7	-4.3	-5.3	-110.8
Cast iron	-1.1	-1.7	-2.2	- 18.3

Example 2

45%	of potassium formate
2%	of potassium hydroxide
2 %	of sodium metabisulfite
0.1%	of 1H-benzotriazole

Comparison Example 2

45% of potassium formate
2% of potassium hydroxide
0.1% of 1H-benzotriazole

Corrosion values according to ASTM D 1384-94 (material removed in g/m²)

	Example 2		Comparison Example 2	
Metal	undiluted	diluted 1:1	undiluted	diluted1:1
Copper	-0.9	-1.6	- 6.1	-25.0
Brass	-2.2	-2.7	-33.2	-42.0
Steel	-1.2	-1.2	- 6.9	- 1.0
Cast iron	-1.3	-1.9	-11.2	-42.6

Example 3

46% of potassium formate
3% of potassium carbonate
1.5% of sodium sulfite
0.05% of sodium silicate
0.05% of 1H-benzotriazole

Comparison Example 3

46% of potassium formate
3% of potassium carbonate
0.05% of sodium silicate
0.05% of sodium silicate

Corrosion values according to ASTM D 1384-94 (material removed in g/m²)

	Example 3		Comparison Example 3	
Metal	undiluted	diluted 1:1	undiluted	diluted 1:1
Copper	- 0.3	-6.3	-11.3	-15.0
Brass	- 0.6	-5.5	- 4.5	- 6.5
Steel	+0.01	-1.8	- 8.3	- 1.1
Cast iron	- 0.03	-8.5	-15.0	-94.6

Example 4

46% of potassium formate
2% of potassium carbonate
0.5% of borax
2% of sodium sulfite
0.05% of 1H-benzotriazole
0.05% of sodium metasilicate

Comparison Example 4

46% of potassium formate
2% of potassium carbonate
0.5% of borax
0.05% of 1H-benzotriazole
0.05% of sodium metasilicate

Corrosion values according to ASTM D 1384-94 (material removed in g/m²)

	Example 4		Comparison Example 4	
Metal	undiluted	diluted 1:1	undiluted	diluted 1:1
Copper	-0.9	-2.2	- 5.2	- 7.5
Brass	-2.4	-5.9	- 7.5	- 9.6
Steel	-1.6	-0.4	- 0.9	- 4.1
Cast iron	-5.4	-6.2	-33.5	-53.8

The experiments show a marked improvement in the corrosion behavior

with the additions according to the invention of sulfites, particularly on steel and cast iron, but also on nonferrous metals. The degree of frostproofing and the viscosity of the corresponding mixtures can be seen from the following comparison of characteristic data:

Identification number	Pure potassium formate, 50% by weight without inhibitors	Brine according to the invention according to Example 4
Degree of frostproofing	-53 °C	-53 °C
Viscosity at -40 °C	18 mm²/s	24 mm²/s
Temperature stability -40 °C +60 °C	 > 7 days > 7 days	 > 7 days > 7 days

The inhibitor combination added is stable in a temperature range from -40 to +80 °C, that is without deposits or formation of crystals.

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Patent Claims

1. A coolant brine based on 20 to 60% by weight of inhibited alkali metal acetates and/or formates having improved corrosion protection, wherein the coolant brines contain 0.2 to 5% by weight of alkali metal salts of sulfurous acid.

2. A coolant brine as claimed in claim 1, which additionally contains alkaline compounds, nonferrous metal inhibitors or silicates.

3. A coolant brine as claimed in claim 1, which additionally contains alkali metal carbonates, alkali metal hydroxides, alkali metal phosphates or alkali metal carbonates.

4. A coolant brine as claimed in claim 1, which additionally contains triazoles, imidazoles, benzotriazoles or mercaptobenzothiazoles.

5. A coolant brine as claimed in claim 1, which additionally contains silicates.

6. A coolant brine as claimed in claim 1, which contains 0.5 to 3% by weight of an alkaline compound.

7. A coolant brine as claimed in claim 1, which contains 0.02 to 0.2% by weight of nonferrous metal inhibitors.

8. A coolant brine as claimed in claim 1, which contains up to 0.3% by weight of silicates.

9. A coolant brine as claimed in claim 1, which contains 0.5 to 3%

by weight of alkali metal salts of sulfurous acid.

10. A coolant brine as claimed in claim 9, which contains 1 to 2.5% by weight of alkali metal salts of sufurous acid.

11. A coolant brine as claimed in claim 6, which contains 2 to 3% by weight of an alkaline compound.

12. A coolant brine as claimed in claim 7, which contains 0.03 to 0.1% by weight of nonferrous metal inhibitors.

13. A coolant brine as claimed in claim 8, which contains 0.03 to 0.1% by weight of silicates.

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AMENDED SHEET